1698

STOPPING
WATER POLLUTION
AT ITS SOURCE

MISA

Municipal/Industrial Strategy for Abatement

PROTOCOL FOR THE REPORTING

OF ANALYTICAL DATA

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PROTOCOL FOR THE REPORTING OF ANALYTICAL DATA

Report prepared by:

George Crawford and Don King
Laboratory Services Branch
Ontario Ministry of the Environment

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MISA
Protocol Document for the Reporting of
Analytical Data

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PROTOCOL FOR THE REPORTING OF ANALYTICAL DATA

1.0 INTRODUCTION

This section provides an overview of the intent, scope and limitations of this guidance document. Additionally, the user is given an insight of the contents which will serve as a key to the use of this manual.

1.1 **Purpose**

This document presents the requirements of the MISA General Regulation (OR 533/89) with respect to the reporting of analytical data for all analytical test groups (ATG) except those relating to organic characterization ATG 28a, 28b, which are described elsewhere (MOCHA).

1.2 **Scope**

This document addresses the reporting of analytical data including areas of: analytical precision, method detection limits (MDLs), smallest reporting increment, truncation or round-off of measurements and "less than" values. It also addresses the use of remark and method codes.

1.3 **Limitations**

This document defines the principles and protocols related to the reporting of analytical data to the Ministry. Except for a few clearly indicated situations (e.g. MDL's), it does not stipulate how that data must be developed, managed, or maintained within the company or laboratory record system. This approach leaves room for the use of data reporting computer systems and practices which best suit existing conditions.

Information on the use of MIDES is contained in the instruction manual General User's Guide, MIDES - MISA Data Entry System (July 1991) provided with the software. That document addresses the procedures and protocols required for electronic reporting of both effluent and QA/QC data. A similar guide describes the use of MOCHA for reporting organic open characterization data (see section 7.0).

1.4 **Updates/Revisions**

This document will be reviewed on an annual basis, and revised as necessary to incorporate changes that improve clarity or reflect advancement in the understanding of data use and interpretation, based on best scientific judgement and peer review.

1.5 **Format and Content**

Each topic is addressed by the use of relevent keywords, definitions, a brief background discussion, a statement of regulatory requirements and a proposed protocol. Additional notes are provided based on questions which have arisen in the past. Where alternative or optional protocols exist these will be indicated.

2.0 LABORATORY METHOD DETECTION LIMIT (LMDL)

KEYWORDS:

Analytical Repeatability
Method Detection Limit (MDL)
Laboratory Method Detection Limit (LMDL)
Regulation Method Detection Limit (RMDL)
Matrix/Interference Effects

DEFINITIONS:

Analytical repeatability is a measure of the within-batch variability of measurements in the absence of analytical biases/mistakes or unpredictable sample matrix effects.

A **method detection limit** marks the level above which one can conclude that a measured result indicates the presence of analyte in the sample, with a stated risk that this conclusion is false. For the MDL this estimate is based on the analytical repeatability (within-batch standard deviation), and the risk is less than 1%.

The **LMDL** is a laboratory specific method detection limit calculated using the procedure described in the Ontario MOE publication Estimation of Analytical Method Detection Limits (MDL), June 1991.

The **RMDL** values for analytes required under the MISA regulation identify the upper performance limit permitted for the LMDL. RMDL values are listed in the MOE publication Protocol for the Sampling and Analysis of Industrial/Municipal Wastewater, June 1991.

REQUIRED:

The LMDL must be calculated for each regulated analyte using the procedure described in the Ontario MOE publication Estimation of Analytical Method Detection Limits (MDL), June 1991.

The value of the LMDL for each regulated analyte must be recorded to 2 significant figures (e.g. 0.032) and reported to the Ministry, along with a method code for the test procedure used (see also Method Code).

The measured LMDL must not exceed the RMDL performance criteria.

Laboratories must report all results equal to or greater than their measured LMDL.

NOTES:

The statistical procedure and concepts on which the detection limit is based may NOT incorporate allowance for errors or bias in measurement due to sample [matrix effects] or otherwise. If the result for a specific sample is suspect because of sample matrix effects the analyst may use one of several remark codes to indicate this. If these effects prevent measurement of an analyte, the analyst must estimate the level at which the interference prevents analysis. (see also Reporting Low-Level Data).

The fact that the LMDL is not greater than the RMDL must be demonstrated at least once. The analyst should demonstrate reliable precision before estimating the LMDL. Anomalous values should not be included in the calculation of analytical repeatability. The LMDLs are to be reported using the number of significant digits used in reporting subsequent sample data generated by that analytical method (usually 2 figures, e.g. 0.032). It is recommended that the LMDL be recalculated approximately every 6 months and that the associated documentation be retained, unless routine QC data demonstrate that no significant change has occurred in the sensitivity or the precision of the procedure. The LMDLs must be re-determined whenever a method is changed.

The test samples must be processed individually through the entire method including any pre-treatment. The analytical method must be defined rigourously enough to ensure that replicate measurements will be more or less 'normally distributed' i.e. clustered together. If the method is modified, a new LMDL must be determined for each affected analyte.

The size of sample analysed, and associated changes in dilution/concentration factors, affect the LMDL value proportionately. Therefore the LMDL should be determined using the routine sample aliquot and dilution factor that will be applied when analysing actual samples.

LMDLs must be determined using the exact analytical procedures to be used for MISA samples. If samples normally contain high concentrations of target parameters and the RMDL cannot be achieved using the sample volume or dilution factor normally used, the sample extract may be concentrated or a larger sample volume used to determine the LMDL. In this case any MISA sample found to contain "non-detectable" levels of target parameters at the normal dilution must be concentrated by the same factor as was used for the LMDL determination or by a factor which allows the parameters to be detected.

3.0 ROUTINE DATA REPORTING - METHOD CODES

KEYWORDS: Method code

DEFINITIONS: The method code is a six character alphanumeric code (e.g. ID000A) including two characters to identify the laboratory and four characters to identify the test method. The code is defined by the laboratory using a laboratory ID code provided by the Laboratory Services Branch.

REQUIRED: The company must report to the Ministry the names of its laboratories including sub-contracted associations, contact information, and an analytical method code and its corresponding LMDL(s) for each analytical procedure that might be used for reporting MISA test data.

Laboratories are required to document and follow the test procedures selected, and to apply the specified quality assurance and quality control practices.

Any significant changes to the method which might affect the precision, accuracy, or recovery of the method must be documented by the laboratory and reported to the company and the Ministry along with new estimates of the LMDL.

PROTOCOL: The company contacts the specialist within Water Resources Branch, MISA Office, for the appropriate Ministry Sector to request the laboratory ID codes, which are assigned by LSB, for its internal and contract laboratories.

The laboratory lists each of its methods for the MISA analytical tests for which it is responsible, and assigns a unique method code for each of the variations/combinations of sample preparation, analytical procedure and measurement detection system.

The method code includes the assigned ID code plus four characters such as 001A, 023C, etc., to reflect a method number (001) and a version (A). The minimum documentation for a method used to determine one or more tests might include:

CODE	Brief Description
ID003A	(sample prep).....entire sample (analytical workup).....acid digestion (detection system).....AAS

The laboratory must maintain a complete procedural description of the method and associated control practices for review by Ministry staff on request.

A form for reporting method codes and LMDL's is included in the Ministry document Guidelines for Preparing an Initial Report.

NOTES:

Many commercial and industrial laboratories have already been assigned their ID code and have prepared their lists of methods and method codes.

Changes in the detection system often involve a change in the physical principles and therefore affect the type and severity of interferences encountered. They may also affect precision and accuracy. The method code should reflect this, for example, code ID009A = AAS whereas ID009B = ICP.

Analysts should also participate in relevant interlaboratory comparison studies, as available, and analyze suitable certified reference materials (as available), to ensure the overall validity of their data.

MIDES includes a table of LMDL's and default method codes which must be filled in by the company prior to using MIDES. If the method used is different than the default, the correct method code must be entered at time of data entry.

3.1 ROUTINE DATA REPORTING - SIGNIFICANT DIGITS

KEYWORDS: Analytical Repeatability
Laboratory Method Detection Limit (LMDL)
Significant Digits
Smallest Reporting Increment (SRI)

REQUIRED: Laboratories must report all results equal to or greater than their predetermined Laboratory Method Detection Limit (LMDL).

Results should be reported with at least two significant digits. (see notes below).

PROTOCOL: Calculate the precision (standard deviation) of the analytical method by one of the alternatives provided in the Ontario MOE publication Estimation of Analytical Method Detection Limits (MDL), June 1991.

Determine SRI value, thus:

SRI = Standard Deviation rounded down to nearest 1, 2, or 5

Thus if the first (leftmost) digit of the estimated standard deviation is

5 or greater;	SRI = 5
2, 3 or 4;	SRI = 2
1;	SRI = 1

Example:

Standard Deviation	SRI
570	500 !
293	200 !
134	100 !
0.038	0.02
0.013	0.01
0.0088	0.005

! Right hand zeros may not be significant since they are also required to indicate the position of the decimal.

Results are reported in multiples of SRI. e.g. if SRI = 0.2, results are reported in steps of 0.2, thus ..., 6.4, 6.6, 6.8, ...

Report analytical results to the nearest SRI or to retain at least two significant digits. Three significant digits are required if the first digit on the left is a '1'.

Ensure that the units of measure are correct. Add any appropriate remark codes, and correct the default method code if necessary.

NOTES:

For the purposes of the MISA regulation two significant digits are required for most data. If result = 2.234 and SRI = 0.002 only the first two digits (2.2) are required.

Results should be reported in steps not larger than the SRI, unless at least two significant digits can be retained.

In the absence of a measurable response at or above the LMDL, or for problems regarding sample matrix, see the issue of 'Reporting Low-Level or Less-Than Data'.

Estimates of standard deviation, and therefore of LMDL and SRI, are affected by the size of the sample aliquot and any additional dilution or concentration factors. Thus, if SRI =0.002 and a 100X dilution of sample is taken, then the SRI becomes 0.2

While the SRI may be determined by the above protocol the laboratory is free to choose a lower SRI. The selected SRI must not be greater than the analytical standard deviation.

4.0 LOW-LEVEL AND LESS-THAN DATA REPORTING

KEYWORDS: Regulation Method Detection Limit (RMDL)
Laboratory Method Detection Limit (LMDL)
Smallest Reporting Increment (SRI)

DEFINITIONS: The following examples explain the usage of '<' symbol in front of a reported value when reporting 'less-than', and the remark codes used to discriminate between various types of less-than and low-level data. For these examples, assume that RMDL = 25, LMDL = 7.3, SRI = 2.

Less Thans (Interference)

A result cannot be obtained because of sample matrix interference effects, etc. Report an estimate of the upper limit for the effect of interference with a < in front of the value and the remark code <:

e.g. < 150 <

Low-Level (Below RMDL but not below LMDL)

The company/laboratory is <u>required</u> to report results in this range but may qualify them as <u>low-level</u> using the remark code <T:

e.g. 12 <T

Less Thans (Measurements Censored Below LMDL)

The company/laboratory may choose NOT to report results when they are below LMDL. MISA requires the value of LMDL be reported with a < in front and remark code <DL:

e.g. < 7.3 <DL

Very Low-Level (Below LMDL but not below SRI)

The company/laboratory may choose the option to report results in this range and may qualify them

as very low-level. Report the result and remark code <DL:

e.g. 3 <DL

Less Thans (Below SRI or Below 1/10th RMDL)

The company/laboratory chooses to report results which are below LMDL and obtains either no measurable response or a result which is very low compared to the needs of the MISA program. These are considered as 'analytical zeros'. Report the value of SRI with a < in front and remark code <W:

e.g. < 2 <W

REQUIRED: A result must be reported for all regulated analytes.

All results at or above the LMDL must be reported. If the company chooses NOT to report results below LMDL, it must report the value of LMDL preceded by a < sign and accompanied by the remark code <DL. The LMDL value should usually be reported to two figures.

PROTOCOL: All results above RMDL may be accompanied by an appropriate explanatory remark code.

Results at or above LMDL but below RMDL may be accompanied by the remark code <T.

Results below LMDL need not be reported. (see required above).

Results below LMDL but at or above SRI may be reported, accompanied by the remark code <DL, without a < in front of the result.

Results below LMDL (where LMDL is below RMDL/10) or results below SRI, (where SRI is not greater than LMDL/3), may be reported as the value of RMDL/10 or SRI (as appropriate) preceded by < and accompanied by the remark code <W.

NOTES:

In the absence of a result due to misadventure, or in the absence of an estimate of the interference limit due to sample matrix effects, the analyst must provide an explanation for the lack of a result by an attached report, and/or by use of an accepted remark code.

When the analyte cannot be measured, the analyst should provide an estimate of the minimum level of analyte that might have been measurable. This estimate is preceeded by a < sign and accompanied by the remark code <.

THE REMARK CODES <, <T, <DL, AND <W HAVE PRIORITY OVER ALL OTHER REMARK CODES WHEN REPORTING VALUES THAT REQUIRE THEIR USE.

The practice to report or not to report results below LMDL should be applied consistently once the decision has been made.

The MIDES data reporting system permits the use of a 'hot-key' to automatically enter less-thans when the measured value is below LMDL. (The LMDL values must first be entered into the MIDES LMDL table.) The hot-key causes the screen to display:

result	remark
< LMDL	<DL

For example, if LMDL = 17 and the measured value was 6, the screen would automatically show:

< 17	<DL

The data entry person can overide the < LMDL with the actual measured result when choosing to report results below LMDL. The <DL remark should remain.

Thus, the screen could be changed to show:

6	<DL

If the result was below 5 (SRI), the data entry person would then have to change both the result and the remark fields:

< 5	<W

5.0 REMARK CODES FOR DATA REPORTING (GENERAL)

KEYWORDS: Remark Codes
Attached Reports
Laboratory Method Detection Limit (LMDL)

DEFINITIONS: Three-character remark codes are provided in the MIDES data reporting system as a means for qualifying reported results or to explain the absence of a result.

REQUIRED: An analytical result must be reported for all regulated analytes when the result is at or above the LMDL. When no result is available, a written explanation must be provided.

The remark code <DL is required when censoring results below the LMDL. The value of the LMDL is reported preceeded by a < sign and accompanied by the remark code <DL.

NOTES: **The use of a remark code does not preclude the acceptance and use of the reported value by the Ministry.**

Lists of the codes are included in the MIDES manual. Extended definitions are included here to facilitate a more consistent usage. The remark codes are grouped as follows:

- Less than - Low Level Data
- Missing Data - Attached Report
- Sample Matrix Effects/Interference
- Approximate/Unreliable Data
- Compliance Problems - Miscellaneous

5.1 REMARK CODES - LESS THAN - LOW-LEVEL DATA

KEYWORDS: <, <T, <DL, <W, (<WE, <TE)

DEFINITIONS:

< **Actual result less than reported**
The reported value is preceeded by a < sign. No result is available due to matrix effects or excessive dilution. The sample does not contain more than the stated amount.

<T **A measurable trace amount, interpret with caution**
Reported value = measured value.
Value is at or > LMDL but < RMDL.
It is a tentative low-level result.

Such data requires verification against other related data. Even when results exceed the LMDL other QA/QC information may indicate the presence of biases which will affect the interpretation of this data.

<DL **Reported value = or <MDL, measured amount <MDL (non-zero)**
If reported value is preceded by < sign, the reported value = LMDL, and the measured value has NOT been reported.

If reported value is NOT preceded by < sign, the reported value = measured value, but the value is below the LMDL. It is a very low-level result.

Sufficient data of this type may assist in distinguishing between analytes which are consistently absent from those which tend to be found at low levels. This is important when evaluating for the trace presence of analytes of concern, particularly when the levels are comparable to the blank. Conclusions are subject to evaluation of QA/QC blank and spike recovery data.

<W No measurable response (zero) the reported value is the smallest observable response.

The reported value is preceeded by a < sign. Either the measured result was 'analytically zero' and no response was observed, or the response is negligible for the purposes of the MISA regulation. Sufficient data of this type suggests the absence of analyte at levels above the reported value, subject to evaluation of QA/QC spike recovery data.

5.2 REMARK CODES - MISSING DATA - ATTACHED REPORT

KEYWORDS: ?, !, !IN, !NM, AR

DEFINITIONS:

? **Late data: data not yet available: see text**
All available data must be reported within the specified deadline in order to be in compliance. If some data is not yet available from the laboratory a reason must be given.

! **No data will be reported: see textual report**
Field or laboratory accidents may prevent analysis for one or more analytes. Whenever possible fresh samples must be taken to compensate. (see guidelines on sampling and analysis).

!IN **No data:insufficient volume due to inspection**
When MOE inspectors remove some or all of the routine sample, the company is not required to provide analytical data.

!NM **No data: no effluent - no sample available**
If there is no effluent flow there can be no data.

The following code may also be used when a result is being reported

AR **Attached report**
If there is need to explain data, or the lack of data, in more depth than permitted by the use of remark codes, an attached report can be useful. (i.e. this is the code to use to describe the type or nature of poly-chlorinated biphenyls found, (if any).

5.3 **REMARK CODES - SAMPLE MATRIX EFFECTS/INTERFERENCE**

KEYWORDS: I, IB, IC, IM, MP, <, >

DEFINITIONS: The following interference codes are used when a result IS being reported.

I **Interference suspected**
The nature of the sample, problems during sample preparation or analysis, etc. lead the analyst to question the result. Do not use this remark indiscriminately.

IB **Interference: background**
Often relates to problems setting background correction, baseline, etc., due to noise or adjacent interfering peaks.

IC **Interference: colour**
Certain colourimetric tests may yield high results on coloured samples.

IM **Interference: Sample matrix**
Often relates to interanalyte effects which affect response factors. (e.g. coelution)

MP **Multiphase sample: result may be suspect**
The presence of fine and coarse particulates and/or an oily phase, or biomaterial, wood chips, etc., may prevent the achievement of a representative sample.

< **Actual amount less than reported**
When a result is not available due to interference the analyst should estimate and report an estimate of the 'sample detection limit' (interference limit). The estimate is preceeded by < and accompanied by the remark code <.

> **Actual amount greater than reported**
The analyst suspects that the response is suppressed by severe interference effects.

5.4 REMARK CODES - APPROXIMATE/UNRELIABLE DATA

KEYWORDS: A, AIS, UCR, UNF, UQC, USD

DEFINITIONS:

A **Approximate value**
The result is less precise or less accurate than usual, i.e. the nature of the sample prevents proper representative aliquotting.

AIS **Approximate value: Insufficient sample**
Smaller than routine aliquots degrade the precision and reliability of measurements.

UCR **Data unreliable: could not confirm by reanalysis.**
When a suspicious result is obtained the analyst will often repeat the analysis if there is sufficient sample. This indicates inability to reanalyse.

UNF **Data unreliable: container not filled to top**
Tests for many organics require a completely filled container to avoid loss into the headspace. Results will tend to be low.

UQC **Data unreliable: possible lab QC problems**
Tests for some analytes require use of the entire sample. Repeat analysis is not possible to permit correction of QC problem.

USD **Data unreliable: sample decomposition noted**
Certain analytes are particularly perishable especially when the sample is known to have changed in transit to the laboratory. (see also the code OLD to indicate excessive delay before analysis.

5.5 REMARK CODES - COMPLIANCE PROBLEMS - MISCELLANEOUS

KEYWORDS: OLD, SD, SID, SIP, Txx,

DEFINITIONS:

OLD **Old: sample exceeds maximum storage time**
The regulatiion specifies a maximum storage time before analysis. Exceeding this time may not affect results, but should be noted.

SD **Sample duplicates differ in appearance**
Field duplicates are required under the regulation to monitor the variability and reliability of sampling. When the samples look different upon arrival at the laboratory, there may be problems with sampling, transportation, or sample preservation.

SID **Sample identification questionable**
The labels don't match the submission form or the sample appears to be different than expected for the specified source.

SIP **Sample improperly preserved**
The regulation specifies the type of sample preservation required. Analyses may have been performed on a differently preserved, or unpreserved sample, because of misadventure to the proper sample. The analyses should not be done unless there is reason to believe that the result will not be significantly affected.

6.0 REPORTING OF LABORATORY QC SAMPLE DATA

KEYWORDS: Laboratory QC
Bench QC, Run QC
Summaries
Blanks, spiked blanks, spiked samples, replicates

REQUIRED: Every laboratory providing results to the MISA program must prepare a summary report of their bench or run QC data. This summary must include at least the following information for each sample type (blanks, spiked blanks, spiked sample, replicate) as applicable:

- number of actual MISA effluent samples analysed
- number of QC samples (of each type) analysed
- concentration of test analyte found
    - minimum
    - maximum
    - average
- standard deviation of concentrations found
- for spiked blank and/or spiked sample results, the design value of the spike plus minimum, maximum and average recovery
- for replicate samples the standard deviation calculated from the difference between paired results.

$$S = \frac{(D^2)}{2n}$$

Individual reports must be prepared on a quarterly basis (every 3 months) with a final annual summary report every 12 months. All reports must be available for review by Ministry regional or laboratory staff.

An example of data tabulation/presentation is shown in figure 1.

DISCUSSION: The Ministry of Environment must be able to readily access bench level QC data for the purposes of database evaluation and development of appropriate response to effluent data variability.

The information will be coupled with the laboratory specific results obtained from interlaboratory studies to increase the effectiveness of the Ministries performance management activities.

7.0 MOCHA

The MOCHA (Ministry MISA Organic Characterization) data reporting system, is to be used by industry or industry's laboratories to report organic characterization data to the Ministry. This program is supplied on 5 " floppy disks and executes on IBM compatible microcomputers running MS-DOS version 3.3. The MOCHA program generates both hard-copy and computer disk output. These items, along with a transmittal sheet, are to be forwarded to the Ministry"s regional or district office in a manner analogous to that used when reporting MISA target compound data using the MIDES system.